LOCAL EQUILIBRIUM AND OFF-EQUILIBRIUM PHENOMENA IN SILICON QUANTUM WIRES

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ABSTRACT. Charge transport phenomena can been tackled in silicon quantum wires using a subband hydrodynamic model. This has been formulated by closing the moment system derived from the Schrödinger-Poisson-Boltzmann equations on the basis of the Maximum Entropy Principle. The model can be used to deal with thermoelectric effects in Local equilibrium and off-equilibrium regimes.

1. Introduction

In the last decades nanotechnologies made possible the production of innovative devices, such as silicon nanowires (SiNWs) which are largely investigated for the central role assumed by silicon in semiconductor industry. SiNWs have been assembled as field-effect transistors (FETs) Singh *et al.* 2006; Guerfi and Larrieu 2016, logic devices Mongillo *et al.* 2012, thermoelectric coolers Pennelli and Macucci 2013; Pennelli 2014, nanosensors Cao *et al.* 2014, light-emitting diodes and lasers. When the physical size of the system becomes small enough, quantum effects on electronic properties become important and then a description via quantum mechanics is required. These quantum effects arise in systems which confine electrons to regions of dimensions comparable to their de Broglie wavelength. In a nanowire (NW) the electronic states become subject to quantization in the two-dimensional transversal section, and the transport is due to the one-dimensional electron gas in the longitudinal dimension. Under extreme scaling of the device's dimensions (diameters even down to 3 nm), the atoms in the cross section will be countable, and crystal symmetry, bond orientation, and quantum mechanical confinement will matter. Proper atomistic modeling is therefore essential in understanding the electronic band structure of these ultra-scaled cross section nanowire devices Nehari *et al.* 2006. Moreover, if the longitudinal dimension is smaller than 10 nm, tunneling phenomena play an important role necessitating full quantum transport simulations based on the Non-Equilibrium Green's function formalism Aldegunde *et al.* 2011 or the quantum-kinetic Wigner transport equation Yamada *et al.* 2009; Muscato and Wagner 2016; Nedjalkov *et al.* 2018. But, if the scaling is not aggressive, then transport can essentially be described semiclassically, using multi-subband Boltzmann transport equations (MBTEs) combined with Poisson and Schrödinger

equation solvers for the description of charge and the confining potential Jin *et al.* 2008. Numeric solutions of the MBTEs can be obtained either by using deterministic solvers Ossig and Schürrer 2008 or by Monte Carlo solvers Ramayya and Knezevic 2010 at the expense of large computational effort and statistical noise Muscato *et al.* 2010, 2011, 2013; Romano *et al.* 2015. In this paper we shall pursue another route, i.e. from the MBTEs we shall introduce a consistent, physics-based hydrodynamic model derived from the Maximum Entropy Principle of Extended Thermodynamics. Moreover we shall prove that Thermoelectric Effects (TE) can be conveniently analyzed from a hydrodynamic point-of-view, where the main advantages are i) a consistent thermodynamic framework, ii) an easy inclusion of hot electron effects, iii) the determination of the transport coefficients from first principles. The description of TE, at nanoscale, is very important: in fact the Seebeck effect in nanowires has been recently investigated with the future aim of building thermoelectric devices based on nanowire arrays for energy harvesting and using them in low-power portable electronics and autonomous sensor systems Dimaggio and Pennelli 2018. The plan of the paper is as follows. In Section **2** Transport physics in SiNWs is introduced; in section **3** the Extended hydrodynamic model is described. Low-field transport, Thermoelectric effects and Off-equilibrium regime are respectively dealt with in sections **4**, **5** and **6**. Finally conclusions are drawn in section **7**.

2. Transport physics in SiNWs

In the physics of nanowires, we have to take into account two characteristic dimensions, the longitudinal (channel) and transversal lengths. If the transversal dimension is greater than 5 nm, the Effective Mass Approximation is probably valid Zheng *et al.* 2005. Moreover, the main quantum transport phenomena in SiNWs at room temperature, such as the source-to-drain tunneling, and the conductance fluctuation induced by the quantum interference, become significant only when the longitudinal lengths of SiNWs are smaller than 10 nm Wang and Lundstrom 2002. Therefore for longer longitudinal lengths, semiclassical formulations based on the 1-D Boltzmann Transport Equation can give reliable terminal characteristics when it is solved self-consistently by adding the Schrödinger-Poisson equations in the transversal direction. Regarding to the band structure, in SiNWs it is altered with respect to the bulk case depending on the wire cross-section dimension, the atomic configuration, and the crystal orientation Neophytou *et al.* 2008. In this paper, for the sake of simplicity, we shall consider a single valley model, with an effective mass m^*. For a quantum wire with linear expansion in z-direction, and confined in the $x-y$ plane, the normalized electron wave function $\phi(x,y,z)$ can be written in the form

$$\phi(x,y,z) = \chi_{\alpha z}(x,y)\frac{e^{ik_z z}}{\sqrt{L_z}} \tag{1}$$

where $\chi_{\alpha z}(x,y)$ is the wave function of the α-th subband and the term $e^{ik_z z}/\sqrt{L_z}$ describes an independent plane wave in z-direction confined to the normalization length, with $z \in [0, L_z]$ and k_z is the wave vector number. In the z cross section, the wave function $\chi_{\alpha z}$ satisfy the

Schrödinger equation in the Effective Mass Approximation

$$
\begin{cases}
H[V]\,\chi_{\alpha z}^{\mu}[V] = \varepsilon_{\alpha z}[V]\,\chi_{\alpha z}^{\mu}[V] \\[2em]
H[V] = -\dfrac{\hbar^2}{2m^*}\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2}\right) + U(x,y) - eV(x,y,z)
\end{cases}
\tag{2}
$$

where $U(x,y)$ is the confining potential, e the absolute value of the electronic charge, $\varepsilon_{\alpha z}$ are the subband energies representing the energies admitted in the confined $x-y$ plane. The total electron energy is

$$
E_{\alpha z} = \varepsilon_{\alpha z} + \mathscr{E}(k_z) + E_c
$$

where E_c is the bottom of the conduction band and, in the parabolic band approximation, we have

$$
\mathscr{E}(k_z) = \frac{\hbar^2 k_z^2}{2m^*} \quad .
$$

The electrostatic potential V satisfies the Poisson equation

$$
\nabla \cdot [\varepsilon_0 \varepsilon_r \nabla V(x,y,z)] = -e(N_D - N_A - n)
\tag{3}
$$

where ε_0 is the absolute dielectric constant, ε_r is the relative dielectric constant, and N_D, N_A are the assigned doping profiles (due to donors and acceptors) and $n(x,y,z,t)$ is the electron density, which depends on $\chi_{\alpha z}$

$$
n(x,y,z,t) = \sum_{\alpha} \rho^{\alpha}(z,t)|\chi_{\alpha z}(x,y,t)|^2
\tag{4}
$$

where ρ^{α} is the 1-D density in the α-subband

$$
\rho^{\alpha}(z,t) = \frac{2}{2\pi} \int f_{\alpha}(z,k_z,t)dk_z \quad .
\tag{5}
$$

Equations (2), (3) must be coupled to the MBTEs for the electron distribution functions $f_{\alpha}(z,k_z,t)$ in each α-th subband Ferry *et al.* 2009

$$
\frac{\partial f_{\alpha}}{\partial t} + v_z(k_z)\frac{\partial f_{\alpha}}{\partial z} - \frac{e}{\hbar}E^{eff}\frac{\partial f_{\alpha}}{\partial k_z} = \sum_{\alpha'}\sum_{\eta}\mathscr{C}_{\eta}[f_{\alpha}, f_{\alpha'}]
\tag{6}
$$

where

$$
v_z = \frac{1}{\hbar}\frac{\partial E_{\alpha z}}{\partial k_z} = \frac{\hbar k_z}{m^*}, \quad E^{eff} = \frac{1}{e}\frac{\partial E_{\alpha z}}{\partial z} = \frac{1}{e}\frac{\partial \varepsilon_{\alpha z}}{\partial z}
\tag{7}
$$

are respectively the electron group velocity and the effective electric field. In the low density approximation (not-degenerate case), the collisional operator reads

$$
\mathscr{C}_{\eta}[f_{\alpha}, f_{\alpha'}] = \frac{L_z}{2\pi}\int dk_z' \left\{ w_{\eta}(\mathsf{k}',\mathsf{k})f_{\alpha'}(k_z') - w_{\eta}(\mathsf{k},\mathsf{k}')f_{\alpha}(k_z) \right\}
\tag{8}
$$

where $w_{\eta}(\mathsf{k},\mathsf{k}') = w_{\eta}(\alpha,k_z,\alpha',k_z')$ is the η-th scattering rate. When $\alpha = \alpha'$ we have an intra-subband scattering, otherwise we have an inter-subband scattering. Scattering mechanisms in SiNWs must comprise acoustic phonon scattering, non-polar optical phonon scattering, surface scattering, scattering with ionized impurities, as well as surface roughness scattering: the details of such mechanisms can be found in Muscato *et al.* 2019.

So in principle, one has to solve a complicate system formed by two blocks, the Schrödinger-Poisson equations and the MBTEs. The coupling between the two blocks is due to the subband energies $\varepsilon_{\alpha z}$ (from which one can evaluate the effective field $(7)_2$), the wave functions $\chi_{\alpha z}$ (which enter in the definition of the electron density (4) and in the scattering mechanisms), as well as the linear density (5).

3. The Extended hydrodynamic model

From the MBTEs one can obtain hydrodynamic-like equations. By multiplying the MBTEs by the weight functions $\psi_A = \{1, v_z, \mathscr{E}, \mathscr{E}v_z\}$, and integrating in the k_z space, one obtains the following hyperbolic system of PDEs Muscato and Di Stefano 2012a

$$\frac{\partial \rho^\alpha}{\partial t} + \frac{\partial (\rho^\alpha V^\alpha)}{\partial z} = \rho^\alpha \sum_{\alpha'} C_\rho^{\alpha\alpha'} \tag{9}$$

$$\frac{\partial (\rho^\alpha V^\alpha)}{\partial t} + \frac{2}{m^*} \frac{\partial (\rho^\alpha W^\alpha)}{\partial z} + \frac{e}{m^*} \rho^\alpha E^{eff} = \rho^\alpha \sum_{\alpha'} C_V^{\alpha\alpha'} \tag{10}$$

$$\frac{\partial (\rho^\alpha W^\alpha)}{\partial t} + \frac{\partial (\rho^\alpha S^\alpha)}{\partial z} + \rho^\alpha e E^{eff} V^\alpha = \rho^\alpha \sum_{\alpha'} C_W^{\alpha\alpha'} \tag{11}$$

$$\frac{\partial (\rho^\alpha S^\alpha)}{\partial t} + \frac{\partial (\rho^\alpha F^\alpha)}{\partial z} + 3 \frac{e}{m^*} \rho^\alpha E^{eff} W^\alpha = \rho^\alpha \sum_{\alpha'} C_S^{\alpha\alpha'} \tag{12}$$

in the unknowns (called moments) ρ^α (1-D density), V^α (mean velocity), W^α (mean energy) and S^α (mean energy-flux), and

$$F^\alpha = \frac{2}{(2\pi)} \frac{1}{\rho^\alpha} \int f_\alpha \mathscr{E} v_z^2 dk_z$$

$$C_\rho^{\alpha\alpha'} = \frac{2}{(2\pi)} \frac{1}{\rho^\alpha} \sum_\eta \int \mathscr{C}_\eta[f_\alpha, f_{\alpha'}] dk_z$$

$$C_V^{\alpha\alpha'} = \frac{2}{(2\pi)} \frac{1}{\rho^\alpha} \sum_\eta \int \mathscr{C}_\eta[f_\alpha, f_{\alpha'}] v_z dk_z$$

$$C_W^{\alpha\alpha'} = \frac{2}{(2\pi)} \frac{1}{\rho^\alpha} \sum_\eta \int \mathscr{C}_\eta[f_\alpha, f_{\alpha'}] \varepsilon_z dk_z$$

$$C_S^{\alpha\alpha'} = \frac{2}{(2\pi)} \frac{1}{\rho^\alpha} \sum_\eta \int \mathscr{C}_\eta[f_\alpha, f_{\alpha'}] \varepsilon_z v_z dk_z.$$

The above moment system is not closed: there are more unknowns than equations. The Maximum Entropy Principle (MEP) leads to a systematic way for obtaining constitutive relations on the basis of the information theory, as already proved in the simulation of 3D electron transport in sub-micrometric devices in the case in which the lattice phonons are considered as a thermal bath with constant temperature Mascali and Romano 2017b or when the phonons are off-equilibrium Muscato and Di Stefano 2008, 2011a,b,c,d, 2012b; Mascali 2015; Muscato and Di Stefano 2015; Mascali 2016; Mascali and Romano 2017a, in 2D nanoscale structures Camiola *et al.* 2012, 2013; Mascali 2017. We define the entropy

of the electron system as Mascali and Romano 2010

$$S_e = \sum_\alpha |\chi_\alpha(x,y,t)|^2 S_e^\alpha \tag{13}$$

$$S_e^\alpha = -\frac{2}{(2\pi)} k_B \int_{\mathbb{R}} (f_\alpha \log f_\alpha - f_\alpha) dk_z. \tag{14}$$

According to the MEP, if a given number of moments M_A^α are known, the distribution function $\hat{f}^\alpha$, which can be used to evaluate the unknown moments, correspond to the extremum of the total entropy density under the constraint that they yield the known moments, i.e.

$$\frac{2}{(2\pi)} \int_{\mathbb{R}} \psi_A \hat{f}_\alpha dk_z = M_A^\alpha. \tag{15}$$

If we introduce a set of Lagrange multipliers λ_A, the problem to maximize S_e under the constraints (15) is equivalent to maximize

$$S' = S_e - \sum_\alpha \sum_A \lambda_A^\alpha |\chi_\alpha(x,y,t)|^2 \left[\frac{2}{(2\pi)} \int_{\mathbb{R}} \psi_A \hat{f}_\alpha dk_z - M_A^\alpha \right].$$

So doing we shall obtain the following distribution function:

$$\hat{f}_\alpha = \exp(-\Sigma^\alpha) \quad , \qquad \Sigma^\alpha = \frac{1}{k_B} \sum_A \psi_A \lambda_A \tag{16}$$

$$\psi_A = (1, v_z, \mathscr{E}, \mathscr{E} v_z) \quad , \qquad \lambda_A = (\lambda^\alpha, k_B \lambda_V^\alpha, k_B \lambda_W^\alpha, k_B \lambda_S^\alpha) \tag{17}$$

By inserting the previous equations in (15), we obtain

$$M_A^\alpha = M_A^\alpha(\lambda_A)$$

which define implicitly the Lagrange multipliers as functions of the basic moments. However such a procedure requires a numerical inversion, which is not practical for numerical simulations of electron devices, since it must be performed at each time or iteration step. In order to invert the above relations, one assumes a small anisotropy in the distribution function Mascali and Romano 2010; Camiola *et al.* 2012; Mascali 2016; Mascali and Romano 2017b by introducing the smallness parameter τ. We shall assume that the multipliers are analytic in τ and expand them around $\tau = 0$ up to the second order and, taking into account the representation theorem for isotropic function, we have

$$\lambda^\alpha = \hat{\lambda}^\alpha + \mathcal{O}(\tau^2), \quad \lambda_W^\alpha = \hat{\lambda}_W^\alpha + \mathcal{O}(\tau^2) \tag{18}$$

$$\lambda_V^\alpha = \tau \hat{\lambda}_V^\alpha + \mathcal{O}(\tau^2), \quad \lambda_S^\alpha = \tau \hat{\lambda}_S^\alpha + \mathcal{O}(\tau^2) \tag{19}$$

therefore, up to the first order in τ, we obtain

$$\hat{f}_\alpha = \exp\left(-\frac{\hat{\lambda}^\alpha}{k_B} - \hat{\lambda}_W^\alpha \mathscr{E} \right) \left\{ 1 - \tau \left(\hat{\lambda}_V^\alpha v_z + \hat{\lambda}_S^\alpha \mathscr{E} v_z \right) \right\} + \mathcal{O}(\tau^2). \tag{20}$$

We remark that, for $\tau = 0$, the eq.(20) looks like the equilibrium distribution function, supposing to have

$$\hat{\lambda}_W^\alpha|_E = \frac{1}{k_B T_e^\alpha} \tag{21}$$

where T_e^α is the electron temperature. However $\hat{\lambda}^\alpha, \hat{\lambda}_W^\alpha$ are not the equilibrium part of $\lambda^\alpha, \lambda_W^\alpha$, but the part arising in the case $\hat{f}_\alpha$ is isotropic. The Lagrange multiplyers are determined by imposing the constraint (15), and we get

$$\frac{\hat{\lambda}^\alpha}{k_B} = -\log \frac{\rho^\alpha \hbar \pi^{\frac{1}{2}}}{\sqrt{4m^* W^\alpha}}, \quad \hat{\lambda}_W^\alpha = \frac{1}{2W^\alpha} \tag{22}$$

$$\tau \hat{\lambda}_V^\alpha = -\frac{5m^*}{4W^\alpha} V^\alpha + \frac{m^*}{4(W^\alpha)^2} S^\alpha, \quad \tau \hat{\lambda}_S^\alpha = \frac{m^*}{4(W^\alpha)^2} V^\alpha - \frac{m^*}{12(W^\alpha)^3} S^\alpha. \tag{23}$$

By using the distribution function (20), the higher-order flux term F^α has been evaluated

$$F^\alpha = \frac{6(W^\alpha)^2}{m^*} \tag{24}$$

as well as the production terms $C_\rho^{\alpha\alpha'}, C_V^{\alpha\alpha'}, C_W^{\alpha\alpha'}, C_S^{\alpha\alpha'}$. In particular the right-hand-sides of equations (10), (12) can be written as

$$\rho^\alpha \sum_{\alpha'} C_V^{\alpha\alpha'} = \mathscr{A}(\rho^\alpha, W^\alpha) J^\alpha + \mathscr{B}(\rho^\alpha, W^\alpha) J_W^\alpha \tag{25}$$

$$\rho^\alpha \sum_{\alpha'} C_S^{\alpha\alpha'} = \mathscr{A}^\star(\rho^\alpha, W^\alpha) J^\alpha + \mathscr{B}^\star(\rho^\alpha, W^\alpha) J_W^\alpha \tag{26}$$

where $J^\alpha = \rho^\alpha V^\alpha$, $J_W^\alpha = \rho^\alpha S^\alpha$. In the stationary regime the eqs. (10), (12) with (25), (26) can be solved in terms of J^α and J_W^α obtaining

$$J^\alpha = a_{11}(\rho^\alpha, W^\alpha) \frac{\partial \rho^\alpha}{\partial z} + a_{12}(\rho^\alpha, W^\alpha) \frac{\partial W^\alpha}{\partial z} + a_{13}(\rho^\alpha, W^\alpha) \frac{\partial \varepsilon_{\alpha z}}{\partial z} \tag{27}$$

$$J_W^\alpha = a_{21}(\rho^\alpha, W^\alpha) \frac{\partial \rho^\alpha}{\partial z} + a_{22}(\rho^\alpha, W^\alpha) \frac{\partial W^\alpha}{\partial z} + a_{23}(\rho^\alpha, W^\alpha) \frac{\partial \varepsilon_{\alpha z}}{\partial z} \tag{28}$$

and the coefficients a_{ij} can be found in Castiglione and Muscato 2017. Finally we want to stress that the above Extended Hydrodynamic Model has been closed by using first principles, and it is free of any fitting parameters.

4. Low-field transport

When the electric field is small, the system formed by the electrons and the lattice is in Local Thermal Equilibrium (LTE), i.e. the system under study can be split into a collection of sub-systems sufficiently large to allow them to be treated as macroscopic thermodynamic subsystems, but sufficiently small that equilibrium is very close to being realized in each sub-system. The Extended hydrodynamic model can describe the electron system in such regime, supposing to set the smallness parameter $\tau = 0$ and using eq.(21), with the main advantage that the transport coefficients are completely determined without any fitting procedure. In this case , we can obtain the following Gibbs relation (see Appendix A for the details)

$$T_e^\alpha dS_e^\alpha = d(\rho^\alpha W^\alpha) - \bar{v}^\alpha d\rho^\alpha \tag{29}$$

where $\bar{v}^\alpha$ is the chemical potential for the electrons with respect to the energy of the α-th subband (see eq.(??)). From the thermodynamic point-of-view, the lattice can be seen as a

rigid-body endowed with an internal energy density W_L, energy-flux $J^i_{W_L}$, and temperature T_L. The lattice energy balance equation writes

$$\frac{\partial W_L}{\partial t} + \frac{\partial J^i_{W_L}}{\partial x^i} = H_L \tag{30}$$

where H_L denotes the production of internal energy.

Let be S_L the lattice entropy then, in LTE, the Gibbs relation holds

$$T_L dS_L = dW_L. \tag{31}$$

The key point is that, having Gibbs relations, one can define the entropy-fluxes

$$J^{\alpha i}_{Se} = \frac{1}{T^\alpha_e}(J^\alpha_W - \bar{v}^\alpha J^\alpha)z^i, \quad J^i_{S_L} = \frac{1}{T_L}J^i_{W_L} \tag{32}$$

where z^i is the unit vector in the z-direction, and the quantity

$$J^{i\alpha}_h = T^\alpha_e J^{i\alpha}_{Se} \tag{33}$$

is known as electron heat flux density.

If we define the total entropy and its flux as

$$S_{tot} = S_e + S_L, \quad J^i_{Stot} = \sum_\alpha J^{\alpha i}_{Se}|\chi_\alpha|^2 + J^i_{S_L} \tag{34}$$

then, from the moment system, one can write down the total entropy balance equation Muscato 2001

$$\frac{\partial S_{tot}}{\partial t} + \frac{\partial J^i_{Stot}}{\partial x^i} = P_S, \quad P_S = \sum_\alpha P^\alpha_S|\chi_\alpha|^2 \tag{35}$$

$$P^\alpha_S = \frac{J^\alpha z^i}{T^\alpha_e}\frac{\partial \hat{\phi}^\alpha}{\partial x^i} + (J^\alpha_W - \bar{v}^\alpha J^\alpha)z^i\frac{\partial}{\partial x^i}\left(\frac{1}{T^\alpha_e}\right) - \sum_{\alpha'}\frac{\rho^\alpha}{T^\alpha_e}\bar{v}^\alpha C^{\alpha\alpha'}_\rho \tag{36}$$

where the electro-chemical potential is

$$\hat{\phi}^\alpha = -\bar{v}^\alpha + \varepsilon_{\alpha z}. \tag{37}$$

Now we shall suppose that the electrons and the lattice are in local thermal equilibrium with the same temperature T_L i.e.

$$T^\alpha_e = T_L \tag{38}$$

and, from equation (36), we can identify the thermodynamic forces X_α and the corresponding generalized fluxes J_α i.e.

$$X_A = \left\{\frac{1}{T_L}\frac{\partial \hat{\phi}^\alpha}{\partial x^i}, \frac{\partial}{\partial x^i}\left(\frac{1}{T_L}\right), -\frac{\bar{v}^\alpha}{T_L}\right\} \tag{39}$$

$$J_A = \left\{J^\alpha z^i, \sum_\alpha(J^\alpha_W - \bar{v}^\alpha J^\alpha)z^i, \rho^\alpha\sum_{\alpha'}C^{\alpha\alpha'}_\rho\right\} \quad . \tag{40}$$

It is known empirically that, for a large class of irreversible phenomena and under a wide range of experimental conditions, the fluxes are linear functions of the thermodynamical forces Lebon *et al.* 2008, i.e.

$$J_A = L_{AB} X_B \tag{41}$$

and the corresponding phenomena belong to the realm of Linear Irreversible Thermodynamics. In this context, the property of microscopic reversibility for any statistical system near thermal equilibrium give rises to the Onsager Reciprocity Principle (ORP), which states the symmetry of the constitutive matrix i.e.

$$L_{AB} = L_{BA} \quad . \tag{42}$$

Close to local thermal equilibrium, we shall suppose that the electron kinetic energy can be neglected respect to the thermal one

$$W^\alpha \simeq \frac{1}{2} k_B T_e^\alpha = \frac{1}{2} k_B T_L.$$

In this case, from eqs.(27),(28) we can obtain the following relations as function of the variables $(\hat{\phi}^\alpha, T_L)$

$$J^\alpha = b_{11}(\rho^\alpha, W^\alpha)\frac{\partial \hat{\phi}^\alpha}{\partial z} + b_{12}(\rho^\alpha, W^\alpha)\frac{\partial}{\partial z}(k_B T_L) \tag{43}$$

$$J_W^\alpha = b_{21}(\rho^\alpha, W^\alpha)\frac{\partial \hat{\phi}^\alpha}{\partial z} + b_{22}(\rho^\alpha, W^\alpha)\frac{\partial}{\partial z}(k_B T_L) \tag{44}$$

where the coefficients b_{ij} are known functions Muscato and Di Stefano 2012a. The previous equations can be rewritten in terms of the thermodynamic fluxes and forces

$$J^\alpha = T_L b_{11}\frac{1}{T_L}\frac{\partial \hat{\phi}^\alpha}{\partial z} - k_B T_L^2 b_{12}\frac{\partial}{\partial z}\left(\frac{1}{T_L}\right) \tag{45}$$

$$J_h^\alpha = J_W^\alpha - \bar{v}^\alpha J^\alpha =$$
$$T_L(b_{21} - \bar{v}b_{11})\frac{1}{T_L}\frac{\partial \hat{\phi}^\alpha}{\partial z} - k_B T_L^2(b_{22} - \bar{v}^\alpha b_{12})\frac{\partial}{\partial z}\frac{1}{T_L}. \tag{46}$$

Now from the definitions (39),(40) and the eqs.(45), (46) we can identify

$$L_{11} = T_L b_{11}, \quad L_{12} = -k_B(T_L)^2 b_{12}$$

$$L_{21} = T_L(b_{21} - \bar{v}^\alpha b_{11}), \quad L_{22} = -k_B(T_L)^2(b_{22} - \bar{v}^\alpha b_{12})$$

and the ORP (42) implies

$$-k_B T_L b_{12} = b_{21} - \bar{v}^\alpha b_{11} \tag{47}$$

which must be verified numerically taking into account the structure of the wire.

Finally from the previous equations (45),(46) we can identify the electrical conductivity σ^α and the electronic thermal conductivity κ_e^α for the α-th subband with

$$\sigma^\alpha = e^2 b_{11}, \quad \kappa_e^\alpha = -(b_{22} - \bar{v}^\alpha b_{12})k_B. \tag{48}$$

5. Thermoelectric effects

The coupling between temperature gradients and electrical potential gradients gives rise to the Seebeck and Peltier thermoelectric effects. When a small temperature difference ΔT_L is applied to a conductor or semiconductor, the electrons in the hot part have more energy with respect to those of the cold part. As in a neutral gas the charges will diffuse from the hot to the cold part but, since they are charged, this movement produces a current in the material and hence an electric field which opposes to the diffusion. The Thermopower $\mathscr{S}$ (or Seebeck coefficient) is a measure of the voltage produced in the presence of this small temperature difference under the hypothesis of open circuit (i.e. $J^\alpha = 0$), and for each subband is defined as

$$\mathscr{S}^\alpha = \left. \frac{\Delta \hat{\phi}^\alpha}{\Delta T_L} \right|_{J^\alpha = 0}. \tag{49}$$

Then from eq.(27) we have

$$\mathscr{S}^\alpha = \left. \frac{\Delta \hat{\phi}^\alpha}{\Delta T_L} \right|_{J^\alpha = 0} = -k_B \frac{b_{12}}{b_{11}} \tag{50}$$

and we can define the average Thermopower as

$$\mathscr{S} = \frac{\sum_\alpha \rho^\alpha \mathscr{S}^\alpha}{\sum_\alpha \rho^\alpha}. \tag{51}$$

When a small current (or particle flux) passes into an isothermal conductor or semiconductor, a heat current is carried per unit charge through the material. The Peltier coefficient measures this heat current and, for each subband, is defined as

$$\Pi^\alpha = \left. \frac{\partial J_h^\alpha}{\partial J^\alpha} \right|_{\nabla T_L = 0}. \tag{52}$$

The eqs. (45), (46) for $\nabla T_L = 0$ reduce to

$$J^\alpha = b_{11} \frac{\partial \hat{\phi}^\alpha}{\partial z}, \quad J_h^{i\alpha} = \frac{b_{21} - \bar{v} b_{11}}{b_{11}} J^\alpha z^i \tag{53}$$

and since $J_h^{i\alpha} = (0, 0, J_h^\alpha)$ then the Peltier coefficient is

$$\Pi^\alpha = \frac{b_{21}(\rho^\alpha, W^\alpha)}{b_{11}(\rho^\alpha, W^\alpha)} - \bar{v}^\alpha. \tag{54}$$

Moreover, the average Peltier coefficient is

$$\Pi = \frac{\sum_\alpha \rho^\alpha \Pi^\alpha}{\sum_\alpha \rho^\alpha} = \frac{\sum_\alpha \rho^\alpha \left[\frac{b_{21}}{b_{11}} - \bar{v}^\alpha \right]}{\sum_\alpha \rho^\alpha}. \tag{55}$$

Another consequence of the Linear Irreversible Thermodynamics is the Kelvin relation, which relates the Thermopower and the Peltier coefficient by the following relation

$$\Pi^\alpha = \mathscr{S}^\alpha T_L. \tag{56}$$

This relation is easily verified for our model.

In fact, if we substitute (50), (54) into the previous equation, we obtain the eq.(47) and the Kelvin relation is a consequence of the ORP. Hence we have proved that the Extended Hydrodynamic model is able to capture LTE phenomena, without any tuning parameters. In the bulk case, these phenomena are usually described either using phenomenological models or using the Boltzmann transport equation in the relaxation time approximation, where the obtained coefficients weakly depend on the scattering mechanism.

6. Off-equilibrium regime

If the system is not in Local Thermal Equilibrium (i.e. $\tau \neq 0$) the previous results are no more valid. In fact we cannot introduce Gibbs relations in the form (29), and consequently the definitions (32). In this regime we have to use the flux equations (27), (28), and we need another definition for the electro-chemical potential, and the electron heat flux density. That can be achieved by using the Extended Gibbs relation (??) (see Appendix A), which reads

$$\frac{1}{k_B \hat{\lambda}_W^\alpha} dS_e^\alpha = \frac{\hat{\lambda}^\alpha}{k_B \hat{\lambda}_W^\alpha} d\rho^\alpha + d(\rho^\alpha W^\alpha) + \tau \frac{\hat{\lambda}_V^\alpha}{\hat{\lambda}_W^\alpha} d(\rho^\alpha V^\alpha) + \tau \frac{\hat{\lambda}_S^\alpha}{\hat{\lambda}_W^\alpha} d(\rho^\alpha S^\alpha). \tag{57}$$

The coefficient of $d\rho^\alpha$, in analogy to the LTE case (29), can be understood as the off-equilibrium chemical potential and, using the closure eqs.(22), it reads

$$\bar{v}^{\alpha\star} = -\frac{\hat{\lambda}^\alpha}{k_B \hat{\lambda}_W^\alpha} = 2W^\alpha \log\left[\frac{\rho^\alpha \hbar \pi^{\frac{1}{2}}}{\sqrt{4m^* W^\alpha}}\right] \tag{58}$$

and

$$\hat{\phi}^{\alpha\star} = -\bar{v}^{\alpha\star} + \varepsilon_{\alpha z}. \tag{59}$$

Moreover, if we identify $\frac{1}{k_B \hat{\lambda}_W^\alpha} dS_e^\alpha$ with the heat, then the corresponding off-equilibrium heat flux $J_h^{\star i\alpha}$ (up to first order in τ) is

$$J_h^{i\alpha\star} = \left\{\frac{\hat{\lambda}^\alpha}{k_B \hat{\lambda}_W^\alpha} \rho^\alpha V^\alpha + \rho^\alpha S^\alpha + \tau \frac{\hat{\lambda}_V^\alpha}{\hat{\lambda}_W^\alpha} \frac{2\rho^\alpha}{m^*} W^\alpha + \tau \frac{\hat{\lambda}_S^\alpha}{\hat{\lambda}_W^\alpha} \rho^\alpha F^\alpha\right\} z^i \tag{60}$$

and, by using the closure relations (22), (23), (24), we get

$$J_h^{i\alpha\star} = \{J_W^\alpha - (\bar{v}^{\alpha\star} + 2W^\alpha \tau) J^\alpha\} z^i. \tag{61}$$

Using the off-equilibrium chemical potential (58) and eq.(59), we can rewrite eqs. (27), (28) as

$$J^\alpha = b_{11} \frac{\partial \hat{\phi}^{\alpha\star}}{\partial z} + b_{12} \frac{\partial W^\alpha}{\partial z} \tag{62}$$

$$J_W^\alpha = b_{21} \frac{\partial \hat{\phi}^{\alpha\star}}{\partial z} + b_{22} \frac{\partial W^\alpha}{\partial z} \tag{63}$$

therefore we shall be able to define the off-equilibrium Peltier coefficient. If $\nabla W^\alpha = 0$, then from eqs.(62), (63) we get

$$J_W^\alpha = \frac{b_{21}}{b_{11}} J^\alpha.$$

(64)

If we insert this equation into (61), we obtain

$$J_h^{i\alpha\star} = J_h^{\alpha\star} z^i, \quad J_h^{\alpha\star} = \left[\frac{b_{21}}{b_{11}} - (\bar{v}^{\alpha\star} + 2W^\alpha \tau)\right] J^\alpha$$

(65)

from which we can define the off-equilibrium Peltier coefficient

$$\Pi^{\alpha\star} = \left.\frac{\partial J_h^{\alpha\star}}{\partial J^\alpha}\right|_{\nabla T_L = 0} = \frac{b_{21}}{b_{11}} - (\bar{v}^{\alpha\star} + 2W^\alpha \tau).$$

(66)

We notice that this coefficient reduces to (54) if $\tau = 0$. Thus our Extended Thermodynamic model is able to define an off-equilibrium Peltier coefficient, in a larger neighborhood of LTE.

7. Conclusions

We have introduced an Extended hydrodynamic model to be coupled to the Schrödinger-Poisson system, describing transport phenomena in SiNWs. This model is valid in a larger neighborhood of LTE and it is free of any fitting parameters. When the electric field is small, the system formed by the electrons and the lattice is in LTE and the model is able to capture Thermoelectric effects with the main advantage that the transport coefficients are completely determined. Moreover if the system is no more in LTE, taking advantage of Extended Gibbs relations, one can define an off-equilibrium Peltier coefficient. The next step will be the determination of these transport coefficients for realistic SiNWs structures, for which it must take into account the inclusion of the main scattering mechanisms, finite confining potentials, and atomistic calculations for the electronic structure. From the numerical point-of-view the main difficulty is the solution of the Schrödinger-Poisson system (2),(3),(4) that can be tackled according to the guideline in Muscato *et al.* 2018, 2019. These issues are under current investigation and will be the subject of forthcoming articles.

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